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each applicant (underline all surnames)JOHNSON MATTHEY PLC
2-4 Cockspur Street
Trafalgar Square, London SW1Y 5BQ, UK

Patents ADP Number (if you know it) 0851980 3001

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4 Title of the invention

Process for selective hydrogenation of acetylenic compounds
and catalyst therefor

5 Name of Your Agent (if you have one)

GIBSON. Sara Hillary Margaret

"Address for service" in the United Kingdom
to which all correspondence should be sent
*(including the postcode)*Johnson Matthey Catalysts
Intellectual Property Department
PO Box 1, Room N205
Belasis Avenue
Billingham
Cleveland
England, TS23 1LB

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Process for selective hydrogenation of acetylenic compounds and catalyst therefor

The present invention relates to a process for selectively hydrogenating acetylenic compounds in the presence of olefinic compounds. The invention also relates to a novel 5 catalyst suitable for use in such a selective hydrogenation process.

The manufacture of unsaturated hydrocarbons usually involves cracking saturated and/or higher hydrocarbons and produces a crude product containing hydrocarbons that are more unsaturated than the desired product but which are very difficult to separate by 10 fractionation. For example in the manufacture of ethylene, acetylene is a co-product. In polymer-grade ethylene specifications the acetylene content must be less than 10 ppm, typically 1-3-ppm max in the product ethylene, although some plants specify that the acetylene should be < 0.5 ppmv.

15 Because of the difficulty associated with separation of the olefin and acetylene co-products, it has long been the practice in industrial olefin manufacture to remove the acetylenic hydrocarbon product by hydrogenation of the triple bond to form an olefin. This approach carries the risk of hydrogenating the desired product olefin which forms a major component of the feed stream and also of over-hydrogenating the acetylene to produce saturated 20 hydrocarbons. Therefore it is important to choose hydrogenation conditions which favour the hydrogenation of the acetylenic triple bonds but under which the olefinic double bonds are not hydrogenated.

Two general types of gas-phase selective hydrogenation processes for purifying 25 unsaturated hydrocarbons are used. "Front-end" hydrogenation involves passing the crude cracker product gas, from which steam and higher hydrocarbons (C_4+) have been removed, over a hydrogenation catalyst. The crude gas contains much more hydrogen than is required to effect hydrogenation of the acetylenic portion of the feed and therefore the potential for hydrogenation of the olefinic part of the gas stream is high. It is therefore 30 important to choose an appropriately selective hydrogenation catalyst and control the conditions, especially temperature, to avoid unwanted hydrogenation of the olefins. In "tail-end" hydrogenation, the gaseous feed has already been separated from CO_2 and H_2 and so the required amount of hydrogen for the hydrogenation reaction must be introduced into the reactor

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In operating acetylene removal from olefin streams by hydrogenation, it is desirable to avoid hydrogenation of the olefin to a more saturated hydrocarbon. The hydrogenation process is sensitive to temperature, which varies according to the catalyst used. At relatively low temperatures, typically between about 55 and about 70 °C, the acetylene is hydrogenated.

The temperature at which about 99.9% of the acetylene has been hydrogenated is called the "clean-up" temperature (CUT). With a selective catalyst, olefin hydrogenation, which is highly exothermic, begins at a temperature of between 90 and 120 °C, but the availability of hydrogen in the reactor can rapidly lead to thermal runaway and a consequent high level 5 of unwanted olefin hydrogenation. The temperature at which the hydrogenation of olefin begins is called the "light-off temperature" (LOT). Therefore the window of operable temperature, i.e. the difference between the "light-off temperature" and the "clean-up temperature" should be as wide as possible so that a high conversion of acetylene can be achieved whilst avoiding the risk of olefin hydrogenation. This means that a successful 10 catalyst for the selective hydrogenation of acetylenes in an olefin-rich feed gas should provide a high LOT-CUT.

Known catalysts for selective hydrogenation of acetylenes include Pd supported on alumina. US-A-2909578 describes a catalyst comprising Pd supported on alumina, in 15 which the Pd metal is about 0.00001 – 0.0014 percent of the total catalyst weight. US2946829 discloses selective hydrogenation catalysts in which Pd is supported on an alumina carrier having a pore volume of 0 – 0.4 cm³g⁻¹ at a threshold diameter of 800Å or less.

20 US3113980 and US 3116342 describe acetylene hydrogenation processes and catalysts comprising palladium supported on alumina whose pores have a mean radius not less than 100 Å and preferably not more than 1400 Å. The desired physical properties are obtained by heating an active alumina for at least 2 hours at a temperature in the range 800 to 1200°C. US-A-4126645 describes a process of selective hydrogenation of highly 25 unsaturated hydrocarbons in the presence of less unsaturated hydrocarbons characterised by the use of a catalyst which comprises palladium supported on particulate alumina having a surface area in the range 5 to 50 m²g⁻¹, a helium density of under 5 g cm⁻³, a mercury density of under 1.4 g cm⁻³ and a pore volume of at least 0.4 cm³ g⁻¹, at least 0.1 cm³ g⁻¹ of which is in pores of radius over 300 Angstrom units, the palladium being present mainly in 30 the region of the catalyst particles not more than 150 microns beneath their geometric surface.

Whilst most supported Pd catalysts in use are of the "shell" type – i.e. having the Pd present only at or near the surface of the support particles, US3549720 describes the use 35 of catalysts in which the Pd is uniformly distributed throughout the catalyst support, the alumina has a surface area above 80 m²g⁻¹ and the majority of the pores have diameters less than 800 Å. In US4762956, acetylene hydrogenation is carried out over a Pd on alumina catalyst in which the alumina has an average pore radius of 200 – 2000 Å, at least 80% of the pores having a pore radius within the range 100 – 3000 Å and which is formed

by calcining the alumina support material at a temperature greater than 1150°C but less than 1400 °C.

Certain catalysts have been described in the art which contain certain promoters, usually

5 one or more further metal species in addition to the Pd. For example, GB811820 describes acetylene hydrogenation using a catalyst containing 0.001 to 0.035% of palladium on activated alumina also containing 0.001 to 5% of copper, silver, gold, ruthenium, rhodium or iron as a promoter. EP0124744 describes hydrogenation catalysts consisting of 0.1 - 60% by weight of a hydrogenating metal or of a hydrogenating metal compound of subgroup VIII

10 of the periodic system of the elements on an inert support, containing 0.1 - 10% by weight of K₂O and, optionally, 0.001 - 10% by weight of an additive from the group comprising calcium, magnesium, barium, lithium, sodium, vanadium, silver, gold, copper and zinc, in each case based on the total weight of the catalyst, the K₂O doping being applied to a catalyst precursor consisting of the hydrogenating component, the support and, optionally,

15 the additive.

Catalysts comprising palladium and silver on alumina supports are well known for selective hydrogenation of acetylenes and/or diolefins in olefin-containing mixtures and are described in US4409410, for example. In US-A-4504593, the catalysts used are Pd on alumina

20 promoted with germanium, tin or lead. Palladium with 0.005 – 0.1% vanadium on silica or alumina, optionally with a molybdenum compound, was used in GB-A-1302269.

In US-A-4404124 and related patents, the catalyst for selective hydrogenation of acetylenes is a palladium/silver on alumina catalyst in which the palladium is present at or near the surface of the catalyst particle whilst the silver is uniformly distributed throughout the

25 particle. EP0722776 describes a palladium/alumina catalyst including an alkali metal fluoride and silver. US-A-6417136 describes a catalyst composition containing palladium, a catalyst component of either silver or an alkali metal compound, or both silver and an alkali metal compound, and a metal aluminate catalyst support which is prepared by a process of incorporating alumina with a metal component, preferably impregnating alumina with a

30 melted metal component, to thereby provide a metal-incorporated alumina followed by drying and high temperature calcining to thereby provide a metal aluminate catalyst support.

As can be seen from considering the prior art in the field of acetylene hydrogenation, there

35 is a need for an acetylene hydrogenation process and catalyst which is highly selective in order to maximise the conversion of acetylene in an olefin-containing feed, whilst being relatively inactive towards the olefinic bond.

According to the invention we provide a catalyst suitable for use in the hydrogenation of acetylenic compounds to olefinic compounds which comprises palladium supported upon an alumina support material characterised in that said catalyst further comprises a promoter which is selected from a compound of zinc or cerium.

5

The catalyst is active for hydrogenation when the palladium is present in metallic form. The catalyst is usually made by first manufacturing a precursor in which a palladium compound, normally a salt or an oxide, is present on the support. It is normal commercial practice to supply such catalysts in the form of the precursor for reduction of the palladium compound

10 to metallic palladium in situ in the reactor. Therefore according to a second aspect of the invention, we provide a catalyst precursor comprising a reducible palladium compound supported upon an alumina support material characterised in that said catalyst precursor further comprises a promoter which is selected from a compound of zinc or cerium.

15 According to a third aspect of the invention, we further provide a process for the hydrogenation of acetylenic compounds comprising the step of passing a mixture of a gaseous feed containing acetylene and hydrogen over a catalyst comprising palladium supported upon an alumina support material characterised in that said catalyst further comprises a promoter which is selected from a compound of zinc or cerium.

20

The support may be selected from silica, titania, magnesia, alumina or other inorganic carriers such as calcium-aluminate cements. Preferably the support comprises alumina. A preferred alumina support material is predominantly an alpha-alumina. Alpha alumina is already well known for use as a support for palladium catalysts for use in hydrogenation reactions, as described for example in EP-A-0124744, US-A-4404124, US-A-3068303 and other references. It may be made by calcining an active alumina (e.g. gamma alumina or pseudoboehmite) at a temperature of 800 - 1400°C, more preferably 1000 - 1200°C. A detailed description of the effect on the physical properties of alumina of calcining at such temperatures is given in US-A-3113980. Other forms of alumina may be used, for example active aluminas or transition aluminas as described in US-A-4126645. Usually the support (for example an alpha-alumina) has a relatively low surface area. Following the teachings of the prior art, it is preferred that for use in "front-end" hydrogenation the surface area, as determined by the well known BET methodology is less than 50 m²g⁻¹ and more preferably less than 10 m²g⁻¹. The support is preferably of relatively low porosity, e.g. 0.05 - 0.5 cm³g⁻¹. Preferably the mean pore diameter lies within the range 0.05 - 1 micron, more preferably from about 0.05 to 0.5 microns.

The catalyst may be provided in any suitable physical form, but for fixed bed hydrogenation duty, shaped particles having a minimum dimension greater than 1mm are preferred. The

shaped particles may be in the form of cylinders, tablets, spheres or other shapes such as lobed cylinders, optionally with passages or holes. Alternatively, but less preferred are granules. Such particles may be formed by known methods such as tabletting, granulation, extrusion etc. Suitable particle dimensions are selected according to the conditions to be used, since the pressure drop through a bed of small particles is typically greater than through a bed of larger particles. Normally catalyst particles for hydrogenation of acetylene in refinery process streams have a minimum dimension of between about 2 and 5mm, e.g. cylinders of about 3mm diameter and 3mm length are suitable. The catalyst support may be shaped into the desired particle form before the palladium and promoter compound is introduced or alternatively the supported catalyst may be shaped after manufacture. It is greatly preferred to use a preformed shaped catalyst support so that the application of palladium and promoter compound can be controlled to provide non-homogeneous catalyst particles if required. As mentioned previously, supported palladium catalysts are commonly supplied as shell-type catalysts in which the active metal is provided only at or near the surface of the catalyst. In order to achieve such a non-homogeneous distribution it is necessary to apply the active metals compounds after the support particle has been formed. Commercial catalyst supports are readily available in a variety of suitable particle shapes and sizes.

The palladium may be introduced into the catalyst by any suitable method as will be well known to the skilled catalyst manufacturer. A preferred method of manufacture is by impregnation of the support material with a solution of a soluble palladium salt such as palladium nitrate or palladium chloride. The incipient wetness technique is preferred, in which the volume of solution applied to the support is calculated to be sufficient to fill the pores of the support material. The concentration of the solution is adjusted to provide the required amount of palladium in the finished catalyst. The solution is preferably applied by spraying onto the support, normally at room temperature although alternative methods such as dipping the support into the solution may be used. The impregnated support is then dried, and may then be subjected to treatment at elevated temperature to convert the impregnated palladium compound to an oxidic species. For example, when the palladium is applied to the support as a solution of palladium nitrate, the dried, impregnated material is preferably treated at a temperature above 400 °C in order to denitrify the material and form a more stable palladium species which is likely to be mainly palladium oxide.

The palladium is present at a level in the range of about 50 ppm to about 1% by weight but the amount of palladium in the catalyst depends upon the intended use. For removal of acetylenic species from C₂ or C₃ gas streams, the palladium is present preferably at a level in the range of about 50 ppm to about 1000 ppm by weight, calculated on the weight of the total catalyst. More preferably the Pd level for this application is in the range 100 – 500

ppmw. When higher hydrocarbons are to be treated, e.g. in a pygas stream, then the catalyst typically includes a higher loading of palladium, e.g. 0.1% to 1%, more preferably about 0.2% - about 0.8%.

- 5 The promoter compound may be introduced into the catalyst by similar methods to those used for the palladium compound. That is, a solution of a soluble salt of the zinc or cerium compound may be impregnated into the support or sprayed onto the support. Suitable soluble compounds of the promoter include nitrates, basic nitrates, chlorides, acetates and sulphates. The palladium compound and the promoter compound may be introduced onto
- 10 the support at the same time as each other or at separate times. For example a solution of the promoter compound may be applied to a formed material comprising a supported palladium compound. Alternatively a solution containing both a palladium compound and a promoter compound may be applied to the support material. The promoter compound is present at a concentration of 70 – 1500 ppmw based on the promoter metal and the weight
- 15 of the total catalyst. When the promoter is a cerium compound the more preferred concentration is 100 – 600 ppmw. The atomic ratio of Pd to promoter metal is preferably in the range 1:0.5 - 1: 5. The preferred promoter compound is a cerium compound.

A preferred embodiment of the catalyst of the present invention comprises an alumina catalyst support and a palladium compound and a promoter compound, said palladium compound being present at 50ppmw – 500 ppmw based on the weight of the catalyst, said promoter compound being selected from a compound of zinc or cerium and being present at a concentration of 70 – 1500 ppmw based on the weight of the total catalyst.

- 25 The process and catalyst of the invention is useful to remove acetylene and higher acetylenes, for example methyl acetylene and vinyl acetylene from olefin streams. Typical processes operate at pressures between 10 bar and 50 bar (gauge), especially up to about 20 bar. The temperature of operation depends upon the operating pressures but typically operate at inlet temperatures between 40 and 70 °C and outlet temperatures
- 30 between 80 and 120 °C, depending on the requirements of adjacent process steps in the plant.

The process and catalyst of the invention will be further described in the following examples.

35

Examples 1 - 2

A catalyst comprising 230 ppm Pd and the desired amount of the zinc promoter was made by impregnating an alumina support, in the form of 3.2mm pellets, by spraying at room temperature with a calculated volume of an aqueous solution of zinc nitrate and palladium

nitrate sufficient to fill the pores of the catalyst. The concentration of the zinc and palladium in the solution was adjusted to produce a catalyst having the required amount of each metal compound. This method of preparing a supported catalyst compound by the so-called "incipient wetness" method is well known to the skilled practitioner. The resulting material 5 was dried at 105°C in air for 3 hours and then heated to 450 °C in air for four hours to effect denitrification, i.e. to convert the zinc and palladium nitrates to oxidic species. The concentration of the zinc nitrate solution was calculated to provide a pre-determined zinc concentration in the final catalyst. The level of zinc is given in Table 1.

10 Example 3

A catalyst containing cerium instead of zinc was made by the method of Examples 1 and 2 but substituting a solution of cerium nitrate (made using cerium (III) nitrate hexahydrate) for the zinc nitrate.

15 Example 4 – testing of the catalysts

About 20cm³ of whole catalyst pellets (typically 20±1cm³) was accurately weighed and then mixed with 315g of an inert alumina diluent. The catalyst and diluent mixture was then charged to a tubular reactor having an internal diameter of 20mm and a capacity of 200 cm³

20 A model feed gas, designed to simulate de-ethaniser overhead front-end conditions was fed to the reactor at a gas hourly space velocity of 5,000hr⁻¹ at a pressure of 20 bar gauge. The composition of the gas feed was:

Acetylene / mole%	0.6
Carbon monoxide / ppmv	100
25 Ethylene / mole%	30.0
Hydrogen / mole%	15.0
Nitrogen	balance

The catalyst bed temperature was increased in ca. 2.5°C steps to acetylene clean-up (T_{cut}) 30 which was taken to be achieved when the acetylene concentration in the exit gas was <<3ppmv. The experiment was continued by increasing the temperature by 1°C steps until temperature runaway (T_{LOT}). As soon as an exotherm was detected, the reactors were quenched with process nitrogen to aid cooling and thereby flush out the potential reactants. All gas compositions were analysed by gas chromatography.

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By comparing the inlet and exit acetylene levels, acetylene conversion at a given temperature (T_n) was calculated from the following expression:

$$\% \text{ C}_2\text{H}_2 \text{ conv} = [(\text{C}_2\text{H}_2\text{(in)} - \text{C}_2\text{H}_2\text{(out)}) / \text{C}_2\text{H}_2\text{(in)}] \times 100$$

where $C_2H_2_{(in)}$ is the inlet level of acetylene, and, $C_2H_2_{(out)}$ is the outlet (exit) level of acetylene.

Ethylene selectivity (with respect to overhydrogenation) was calculated by the following expression:

$$\%S_{C_2H_4} = 100 - \%S_{C_2H_6}$$

where $\%S_{C_2H_6}$ is the ethane selectivity as defined by the expression below:

$$10 \quad \%S_{C_2H_6} = \{[(C_2H_6)_{out} - (C_2H_6)_{in}]/[C_2H_2]_{in} - (C_2H_2)_{out}\} \times 100$$

Table 1

Catalyst	Promoter	Pd:promoter metal (atomic ratio)	CUT (°C)	LOT (°C)	LOT-CUT (°C)	% C_2H_4 selectivity
Comparison	None		58	100	42	93
Example 1	Zn	1:3	63	120	57	97
Example 3	Ce	1:1	63	120	57	96

15 The selectivity was calculated at the clean-up-temperature for each catalyst. The results show that compared with the unpromoted palladium catalyst, the LOT -CUT operability window is wider and the selectivity to ethylene is significantly better using the catalysts of the invention.

Claims

1. A catalyst suitable for use in the hydrogenation of acetylenic compounds to olefinic compounds which comprises palladium supported upon an alumina support material characterised in that said catalyst further comprises a promoter which is selected from a compound of zinc or cerium.
2. A catalyst as claimed in claim 1 wherein the support is selected from silica, titania, magnesia, alumina, a calcium-aluminate cement or a mixture of these compounds.
3. A catalyst as claimed in claim 2 wherein the support comprises alumina.
4. A catalyst as claimed in any of claims 1 – 3 wherein the mean pore diameter lies within the range 0.05 – 1 micron.
5. A catalyst as claimed in any of the preceding claims wherein the catalyst is in the form of shaped particles having a minimum dimension greater than 1mm.
6. A catalyst as claimed in any of the preceding claims wherein the palladium is present at a level in the range of about 50 ppm to about 1% by weight.
7. A catalyst as claimed in any of the preceding claims wherein the promoter compound is present at a concentration of 70 – 1500 ppmw based on the promoter metal and the weight of the total catalyst.
8. A catalyst as claimed in any of the preceding claims wherein the atomic ratio of Pd to promoter metal is in the range 1:0.5 - 1: 5.
9. A catalyst precursor comprising a reducible palladium compound supported upon an alumina support material characterised in that said catalyst precursor further comprises a promoter which is selected from a compound of zinc or cerium.
10. A process for the hydrogenation of acetylenic compounds comprising the step of passing a mixture of a gaseous feed containing acetylene and hydrogen over a catalyst comprising palladium supported upon an alumina support material characterised in that said catalyst further comprises a promoter which is selected from a compound of zinc or cerium.

Abstract

A catalyst suitable for use in the hydrogenation of acetylenic compounds in an olefin stream comprises a compound of palladium supported upon a support material with a promoter compound selected from a compound of zinc and a compound of cerium.